



# Highly active N-doped carbon nanotubes prepared by an easy ball milling method for advanced oxidation processes



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## ABSTRACT

The performance of novel N-doped carbon materials prepared by an easy ball milling method was evaluated in two distinct advanced oxidation processes (AOPs): catalytic wet air oxidation (CWAQ) and catalytic ozonation (COZ), using oxalic acid as model pollutant. The ball milling method allows the incorporation of large amounts of N-groups onto the surface of carbon nanotubes, namely pyridine-like N atoms (N-6), pyrrole-like N atoms (N-5) and quaternary nitrogen (N-Q), resulting in highly active catalysts for the oxidation of oxalic acid by both AOPs. The material prepared by ball milling with melamine without solvent is the most promising sample, combining an easy preparation with high amount of N-functionalities. Under the operation conditions used, oxalic acid was completely mineralized in 5 min by CWAQ and in 4 h by COZ. The novel metal-free catalyst developed by this easy ball milling method demonstrated to be effective, confirming that this solvent-free methodology is quite adequate for the preparation of N-doped carbon materials with enhanced properties for the mineralization of organic pollutants by the studied processes.

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## 1. Introduction

Noble metals or metal oxides are widely used as the active phases in heterogeneous catalysis, but their application has some drawbacks like high cost, deactivation caused by sintering or poisoning, and harmful impacts on the environment. Therefore, numerous approaches have been attempted to develop high performance metal-free carbon based catalysts as alternatives for the conventional catalysts [1–4]. In the last years, several routes have been tried to modify the carbon structure, in order to develop new functional materials with enhanced properties [5,6].

The introduction of heteroatoms (like N, S or B) with different electronic structures allows the rearrangement of electrons at the carbon surface and changes the properties of the carbon nanotubes (CNTs). The distribution and arrangement of the heteroatoms in the graphitic lattice depends on the synthesis method. Doping can be performed in-situ during the synthesis of the carbon material or ex-situ using appropriate post-treatments. In the case of N-doping, the nitrogen atoms are usually in three different sites of the carbon structure substituting the carbon atoms to form graphitic

(quaternary), pyridinic and pyrrolic structures. N-doping can result in an outstanding performance of the CNTs due to the distribution and arrangement of the heteroatoms on the CNT lattice [1]. Doping with nitrogen significantly improves the catalytic performance of carbon materials, which have been used as metal-free catalysts in oxidation reactions [7,8], dehydrogenation [9], and in oxygen reduction reactions (ORR) in proton-exchange membrane fuel cells [10,11] as catalysts or as catalyst supports.

The increasing concentration of pollutants in water all over the world requires better water and wastewater treatment technologies. Among several technologies available to remove organic pollutants from water, advanced oxidation processes (AOPs) are especially suited when total mineralization of the organic pollutants is the target. Wet air oxidation (WAO) is a technology that can play an important role as primary treatment for highly concentrated wastewaters that are refractory to biological treatments, operating at high reaction temperatures and pressures (200–320 °C and 20–200 bar), which can become milder in the presence of catalysts [12], offering high versatility and efficiency in the abatement of several classes of pollutants and remarkable cost advantages [13,14]. Catalytic ozonation (COZ) is another promising technology for the treatment of organic pollutants [15], operating at room conditions. Single ozonation presents low reactivity towards certain types of recalcitrant compounds and normally leads to an incomplete degradation of the organic pollutants, but remarkable

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**Table 1**

Relevant textural and chemical properties of the carbon nanotube samples tested as catalysts in COZ and CWAQ of oxalic acid.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$(\text{CO})_{\text{TPD}}$ ( $\mu\text{mol g}^{-1}$ )	$(\text{CO}_2)_{\text{TPD}}$ ( $\mu\text{mol g}^{-1}$ )	$N_{\text{XPS}}$ (wt.%)
CNT-O	291	200	23	n.d.
CNT-BM	391	173	44	n.d.
CNT-BM-M-DT	355	338	214	4.8
CNT-BM-M-WT	285	352	144	1.1
CNT-BM-U-DT	353	273	112	0.8
CNT-BM-U-WT	291	405	205	0.3
CNT-BM-M-E	349	394	223	3.1
CNT-BM-U-E	364	347	317	0.2

n.d.-not determined.

improvements can be obtained in the presence of carbon materials [16].

It has been demonstrated that carbon materials are able to enhance the removal of organic pollutants as catalysts in both process catalytic wet air oxidation [17–21] and catalytic ozonation [22–25] due to their outstanding textural and chemical properties. The application of carbon materials as metal-free catalysts provides an alternative to replace catalysts based on noble metals or metal oxides, thus avoiding the leaching of the metals to the liquid phase or over-reduction; in addition, doping with heteroatoms provides increased stability of carbon materials in both acidic and alkaline media [2,26].

Recently, we developed a simple method to obtain carbon nanotubes doped with nitrogen, by ball milling, using melamine and urea as nitrogen precursor followed by appropriate heat-treatment [27]. The procedure is an easy to handle method, avoiding the use of solvents and production of wastes. It does not depend on highly specialized and expensive equipment to manufacture the catalysts, and, therefore, can be easily adopted by industry. This method leads to the incorporation of large amounts of N-groups, namely quaternary nitrogen, pyridinic, and pyrrolic groups. Thus, in this work we evaluate the performance of these novel materials as metal-free catalysts in two distinct AOPs: CWAQ and COZ, using oxalic acid as model pollutant, since it is commonly present as an accumulated final product in several processes of organic pollutants oxidation, including the non-catalytic ozonation and wet air oxidation [28–30]. The main objective of the present work is to study and develop stable, low cost, and efficient catalysts, capable of mineralizing (i.e., totally oxidizing) organic pollutants from water and wastewater.

## 2. Experimental

### 2.1. Materials

Multi-walled carbon nanotubes from Nanocyl (NC3100) were selected as pristine material (CNT-O sample). A ball milled sample (CNT-BM) was prepared in a vibratory Retsch MM200 equipment using the milling conditions determined in a previous work [22]. The milling was performed using zirconium oxide balls and grinding jars. N-doped samples (CNT-BM-M-DT, CNT-BM-M-WT, CNT-BM-U-DT and CNT-BM-U-WT) were prepared in the same apparatus by mixing the pristine CNTs with melamine (M) or urea (U), in the presence or absence of a solvent (wet treatment (WT) or dry treatment (DT) samples, respectively). Additionally, two more samples were doped with nitrogen (CNT-BM-M-E and CNT-BM-U-E) by an external treatment (E), i.e., the N-precursor was mixed with CNT-BM outside the ball milling equipment during 24 h. Finally, the resulting materials were subjected to a thermal treatment under  $\text{N}_2$  flow until  $600^\circ\text{C}$  and kept at this temperature during 1 h. Detailed information can be found elsewhere [27].

### 2.2. Catalyst characterization

The textural characterization of the materials was based on the  $\text{N}_2$  adsorption isotherms determined at  $-196^\circ\text{C}$  with a Quantachrome Nova 4200e apparatus. The nature and amounts of the surface oxygenated groups were determined by temperature programmed desorption (TPD) [31,32], carried out in an Altamira Instruments AMI-300 apparatus. The pH at the point of zero-charge ( $\text{pH}_{\text{pzc}}$ ) was measured by analysis of the pH change of NaCl solutions of different initial values of pH when exposed to samples of the prepared materials during 24 h. The nature and amounts of the nitrogen groups on the surface of the materials were determined by X-ray photoelectron spectroscopy (XPS) using a VG Scientific ESCALAB 200A spectrometer. Additional details can be found in reference [27].

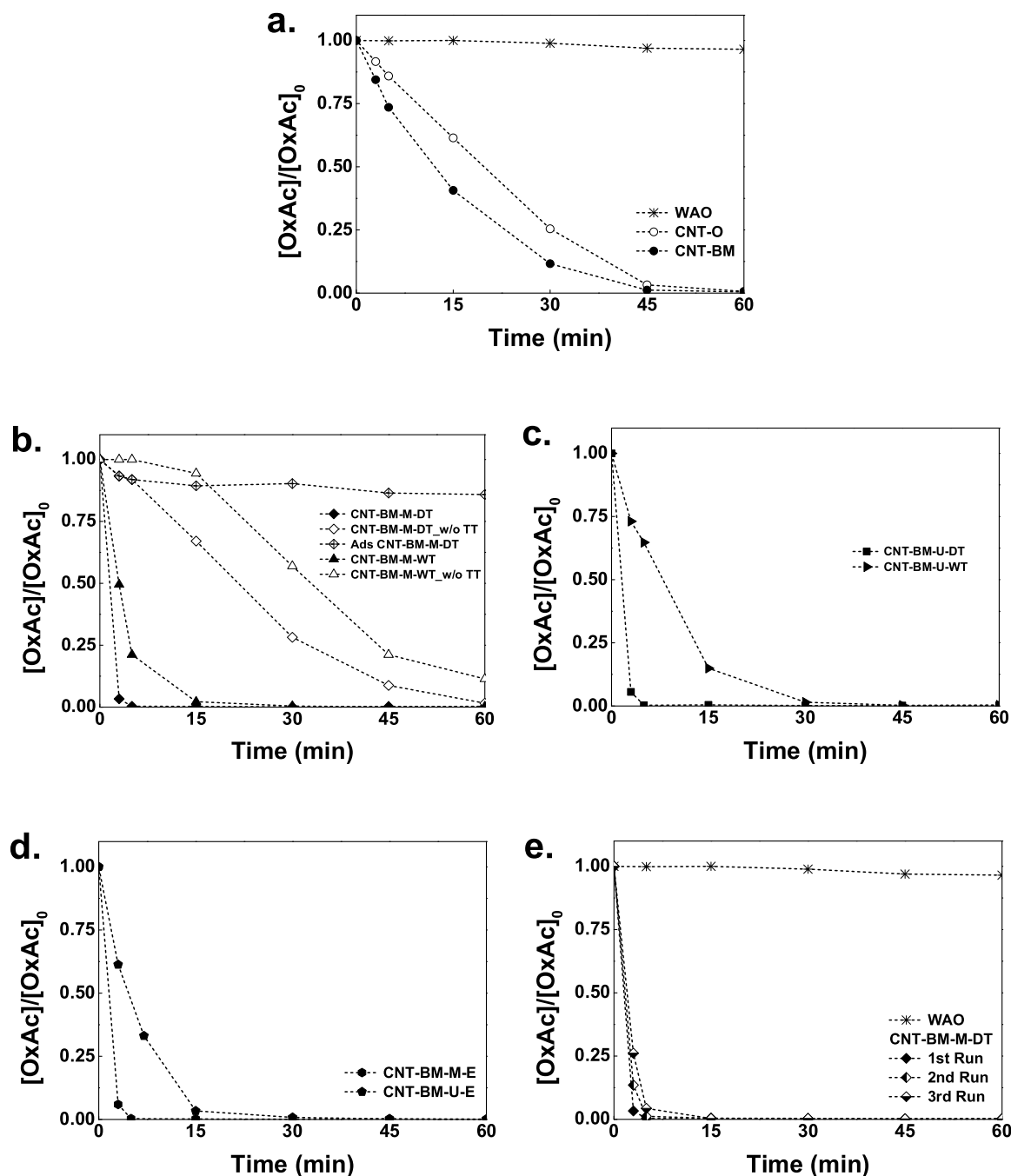
### 2.3. Experimental procedure

CWAQ experiments were performed in a 160 mL 316-SS high pressure batch reactor housing a glass liner (Parr Instruments, USA Mod. 4564). 100 mg of catalyst was added to 75 mL of a  $1000 \text{ mg L}^{-1}$  oxalic acid solution and placed into the reactor. Then, the reactor was flushed with pure nitrogen till complete removal of oxygen, pressurized with 5 bar of nitrogen and then pre-heated up to the desired temperature ( $140^\circ\text{C}$ ) under continuous stirring at 500 rpm in order to ensure proper mass transfer of oxygen in the liquid phase [17,33]. When the desired temperature was reached, pure air was injected to obtain a total pressure of 40 bar inside the reactor (corresponding to 7 bar of oxygen partial pressure); this was considered time zero for the reaction. Reutilization tests were carried out with the CNT sample showing the best catalytic performance, in order to evaluate the stability of the catalyst. At the end of each run, the catalyst was recovered, washed with distilled water and dried at  $110^\circ\text{C}$ . Then, it was tested for a second time using fresh oxalic acid solution. The same procedure was repeated before testing the sample in a third run. In addition, a non-catalytic wet air oxidation (WAO) run was carried out as a blank experiment for the model pollutant, and adsorption experiments were also performed in the autoclave under similar experimental conditions but replacing air by pure nitrogen (40 bar of total pressure).

All COZ experiments were performed at room pressure and temperature, in a stirred semi-batch reactor at laboratory-scale (ca. 1 L). In each experiment, the reactor was filled with 700 mL of a solution containing  $450 \text{ mg L}^{-1}$  of oxalic acid at natural pH (approximately 3). 50 mg of catalyst were introduced into the reactor and kept in suspension by stirring at 200 rpm. Ozone, generated from pure oxygen (in a BMT 802X ozone generator) and monitored (with a BMT 964 ozone analyser), was bubbled into the solution using a diffusor (total flow rate =  $150 \text{ cm}^3 \text{ min}^{-1}$ ; ozone concentration =  $50 \text{ g m}^{-3}$ ). Samples were collected for further analysis using a syringe at selected times. For comparative purposes, both adsorption on the most promising sample and ozonation experiments in absence of catalyst (single ozonation  $\text{O}_3$ ) were also performed in the same system, under identical experimental conditions. In cyclic experiments, the same procedure was followed. After each experiment, the solution was filtered and the CNT sample dried, in order to be used in another run. This procedure was repeated two times (totalizing three consecutive runs). Some experiments were carried out in duplicate and the maximum relative deviation obtained was 2%. The analytical measurements were also performed in duplicate with a maximum relative error of  $\pm 0.5\%$ .

### 2.4. Analytical techniques

Samples periodically withdrawn from the reactors were analysed by high performance liquid chromatography (HPLC) with a



**Fig. 1.** Evolution of the normalized oxalic acid concentrations at 140 °C and 40 bar of total pressure under non-catalytic conditions (WAO), in adsorption experiments (Ads) and by using ball milled carbon nanotubes as catalysts in CWAO (0.1 g of catalyst; initial concentration of 1000 mg L<sup>-1</sup>).

Hitachi Elite LaChrom system equipped with a Diode Array Detector (L-2450). A Bio-Rad Aminex HPX-87H column (300 mm × 7.86 mm) and a H<sub>2</sub>SO<sub>4</sub> solution (4 mM) at a flow rate of 0.6 mL min<sup>-1</sup> (as mobile phase) were used for the determination of oxalic acid concentration. The quantification of oxalic acid was performed at  $\lambda = 210$  nm.

### 3. Results and discussion

#### 3.1. Characterization of ball milled CNTs

The relevant properties of the pristine and ball milled carbon nanotube samples used in the present work are described in Table 1.

More detailed characterization can be found in our previous work [27], where an exhaustive description about the samples characterization is presented and discussed. The methodologies applied ensure the reproducibility of the samples obtained in different batches prepared by the same procedure, with small differences in the surface area ( $\Delta S_{BET} \leq 20 \text{ m}^2 \text{ g}^{-1}$ ) and in the N amount incorporated ( $\Delta N_{EA} \leq 0.1\%$  for the samples with high N-content and  $\Delta N_{EA} \leq 0.03\%$  for samples with low N-content).

In spite of the different treatments applied, the samples show differences in the surface area ( $S_{BET}$ ) lower than  $100 \text{ m}^2 \text{ g}^{-1}$ , even upon the addition of the N-precursors. Ball milling treatment of the pristine CNTs leads to the most significant increase of the surface area (CNT-BM sample,  $391 \text{ m}^2 \text{ g}^{-1}$ ), while the wet treatments result

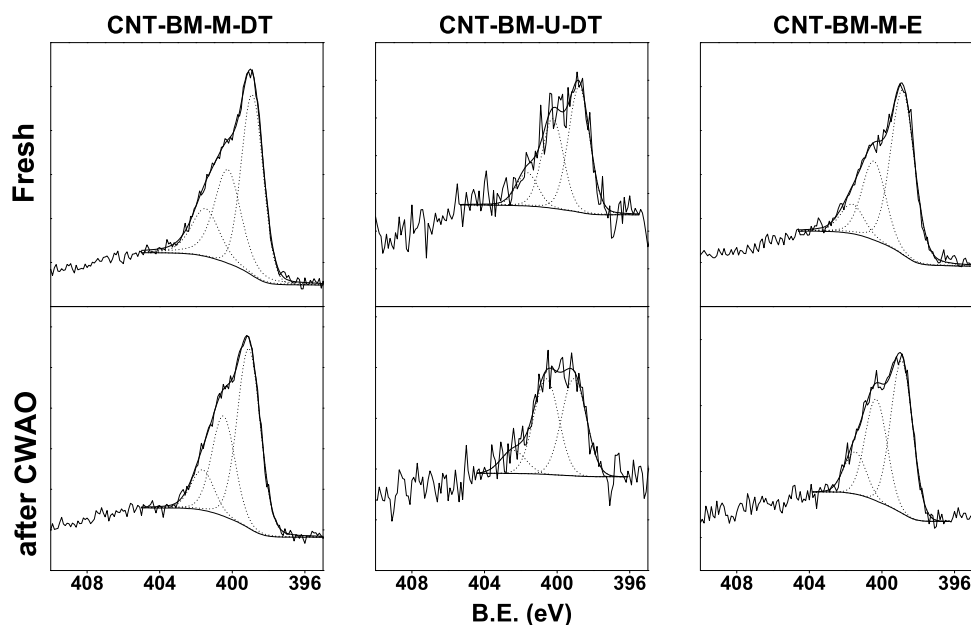


Fig. 2. N1s XPS spectra for some fresh samples and after being used in CWAO of oxalic acid.

in samples with the lowest specific surface areas (CNT-BM-M-WT and CNT-BM-U-WT samples). Regarding the surface chemistry, the TPD results indicate that the ball milled samples are poor in O-containing surface groups, similar amounts of CO and CO<sub>2</sub> being released by all samples. As already reported in a previous work [22], the ball milling treatment does not promote any functionalization of the carbon nanotubes surface with oxygenated groups. However, the addition of the N-precursor reveals a small increase of these groups. Nevertheless, since the samples were thermally treated until 600 °C, only some carbonyl/quinone groups and phenols contribute to the release of CO from the surface, with no contribution of carboxylic acids or anhydrides (since they are removed at temperatures lower than 600 °C). Therefore, all samples present an almost neutral character ( $pH_{pzc}$  between 6.4 and 6.8), due to the incorporation of a significant amount of nitrogen (between 0.2 and 4.8%) on the surface of the CNTs, as determined by XPS analyses. Samples prepared using melamine as N-precursor present higher N contents than those prepared with urea. The use of a solvent during the milling step had a negative effect on the attachment of the N-functionalities, regardless of the precursor used. The nature of the N-functionalities, identified on the materials surface, included pyridine-like N atoms (N-6), pyrrole-like N atoms (N-5), and quaternary nitrogen (N-Q). Since no metals were identified by XPS (results not shown), the samples can perform as metal-free catalysts on different liquid-phase reactions as reported in the next section.

### 3.2. Catalytic tests

The catalytic activity of the CNT samples was evaluated in the oxidation of oxalic acid (used as model pollutant) by catalytic wet air oxidation and catalytic ozonation. Oxalic acid is a refractory short chain carboxylic acid that commonly appears as end-product in several AOPs and it is hardly oxidized under non-catalytic conditions by the selected oxidation processes, representing an adequate probe species to evaluate the processes efficiency.

#### 3.2.1. Catalytic wet air oxidation

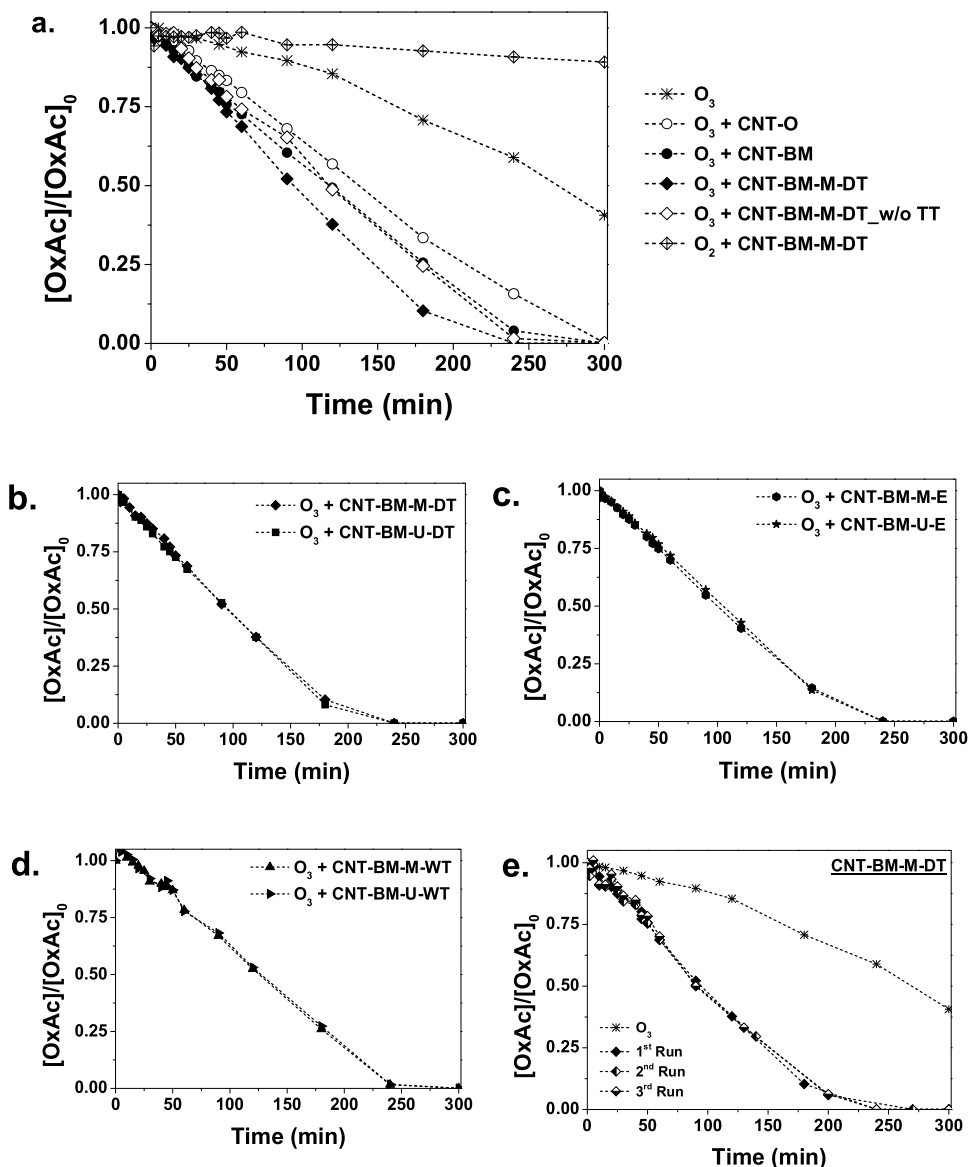
Fig. 1 shows the normalized concentrations of oxalic acid during the reaction time. In the absence of catalyst, oxalic acid is quite

stable and poorly oxidized under the operating conditions used (Fig. 1a, WAO curve). However, total conversion of the model compound is achieved in the presence of the original and the modified CNT samples.

Complete oxidation of oxalic acid can be achieved in less than 60 min using the original CNT sample (Fig. 1a), but a faster removal is observed using the sample CNT-BM. The mechanical treatment performed during ball milling promotes some changes in the nanotubes structure: breaking of the tubes leads to shorter CNTs [34,35], the entanglement of the CNTs decreases, and samples with higher specific surface area and with small particle sizes of agglomerates are obtained [22]. The increase of the available surface area in the CNT-BM sample allows higher amount of active sites, increasing the reaction rate in comparison with the pristine CNTs.

The incorporation of N-groups on the CNTs, using melamine or urea as N-precursors, improves the catalytic activity of the original CNT sample leading to a more rapid degradation of the organic compound. Fig. 1b shows the effect of the thermal treatment applied after the mechanical mixing of the CNTs with melamine under ball milling in the presence/absence of solvent. Without thermal treatment (CNT-BM-M-DT.w/o TT and CNT-BM-M-WT.w/o TT samples) the catalysts underperform compared with the thermally treated ones, suggesting that the presence of pure melamine mixed with CNTs may impair the diffusion of the reactants to the carbon surface where adsorption and reaction take place. In fact, the samples not thermally treated revealed a worse performance than CNT-BM or even pristine CNTs, confirming that the N-precursor hardly contributes to the catalytic activity. According to the deconvolution of the N1s XPS spectrum of the sample CNT-BM-M-DT.w/o TT (not shown), the only N–C bonds present are those characteristic of melamine [27]; therefore, the ball milling of CNTs with melamine does not promote any chemical functionalization of the carbon surface. Thus, the catalytic activity observed for the samples not thermally treated should be credited to the CNTs.

Besides the thermal treatment, the use or not of a solvent (dry or wet treatments) during the ball milling step also results in distinct catalytic performances of the samples. Sample CNT-BM-M-DT leads to an extremely fast removal of oxalic acid, total conversion being observed after about 5 min of reaction, with no contribution of adsorption (Ads CNT-BM-M-DT curve, Fig. 1b), phenomenon that is



**Fig. 3.** Evolution of the normalized oxalic acid concentrations under single ozonation, in adsorption and by using ball milled carbon nanotubes as catalysts in CO<sub>2</sub> (room temperature, 0.05 g of catalyst; initial concentration of 450 mg L<sup>-1</sup>).

negligible during the reaction under the operating conditions used. By using CNT-BM-M-WT sample, the total conversion of oxalic acid is achieved after 15–30 min of reaction. In fact, the samples present significant differences in the amount of N-functionalities (4.8% for CNT-BM-M-DT and 1.1% for CNT-BM-M-WT determined by XPS, Table 1). The use of solvent in the samples preparation, which may restrict the contact between the precursor and the carbon material, revealed a negative effect on the incorporation of N-groups, as discussed with more detail in a previous work [27]. The same was observed when urea was used as N-precursor (Fig. 1c). As observed in the melamine samples, complete conversion of oxalic acid is achieved in 5 min using the CNT-BM-U-DT sample, while around 30 min of reaction are required for full compound mineralization when using the CNT-BM-U-WT sample.

Concerning samples submitted to external treatments, i.e., the N-precursor is mixed with CNT-BM outside the ball milling equipment, the use of melamine as N-source seems to result in a sample with better catalytic performance than urea (Fig. 1d), which may be directly related to the N-content introduced (3.1% against 0.2% determined by XPS for CNT-BM-M-E and CNT-BM-U-E samples,

respectively). However, in any case, both samples lead to complete oxalic acid removal in less than 30 min of reaction. Besides the good performance of the samples obtained by the external treatment, the preparation method involves a dual-step procedure (ball milling of CNTs plus external contact with the N-precursor and solvent). Sample CNT-BM-M-DT combines an easy and simple preparation method without solvent with high catalytic activity for the oxalic acid oxidation by CWAQ. Therefore, more detailed studies were performed using this sample. Fig. 1e shows the normalized oxalic acid concentration during 3 consecutive runs using the same catalyst (CNT-BM-M-DT) with fresh solutions of oxalic acid. The cyclic experiments show a slight deactivation of the catalyst during CWAQ, but, in spite of that, full degradation of oxalic acid is observed in less than 15 min. This is an effect commonly observed during successive runs of CWAQ using carbon samples, and is attributed to a slight oxidation of the carbon surface promoted by the operating conditions used, introducing some acidic groups on the surface which are known to have a negative effect on the catalytic performance of carbon materials in oxalic acid oxidation by CWAQ [8,21]. Nevertheless, the N-groups revealed to be



**Table 2**

Oxygen contents determined by XPS and relative peak contents and positions obtained by N1s spectra fitting of selected samples, before and after CWAQ experiments.

Sample		O <sub>XPS</sub> content (% wt.)	N <sub>XPS</sub> Deconvolution					
			N-6		N-5		N-Q	
			B.E. (eV)	(% wt.)	B.E. (eV)	(% wt.)	B.E. (eV)	(% wt.)
CNT-BM-M-DT	Fresh	0.9	398.9	2.24	400.3	1.66	401.5	0.87
	After CWAQ	1.9	399.1	2.91	400.5	1.62	401.6	0.65
CNT-BM-U-DT	Fresh	0.8	398.8	0.39	400.2	0.28	401.7	0.10
	After CWAQ	2.8	399.1	0.27	400.6	0.26	402.4	0.06
CNT-BM-M-E	Fresh	1.0	398.9	1.86	400.4	0.89	401.6	0.33
	After CWAQ	2.5	398.9	1.36	400.3	0.90	401.5	0.37

stable and there are no significant changes on the N-functionalities after oxalic acid oxidation by CWAQ [36]. Fig. 2 shows the N1s XPS spectra of CNT-BM-M-DT, CNT-BM-U-DT and CNT-BM-M-E before and after being used in CWAQ of oxalic acid. After reaction, the samples kept the original N-functionalities (N-6, N-5 and N-Q groups) with similar proportions; however, a slight increase of the O content was observed in the three cases (from around 0.8 to 1.0% in the original form to 1.9–2.8% after reaction), which is related to the slight oxidation of the surface as discussed above (Table 2).

The obtained results highlight the positive effect of N-groups on the catalytic activity of carbon materials for liquid phase oxidation reactions, as previously reported [8,37–39]. In some cases, linear correlations between the model compound removal rate and the amount of N surface groups have been presented [38,39]. Due to the high catalytic activity of the samples evaluated in this work, especially CNT-BM-M-DT, CNT-BM-U-DT and CNT-BM-M-E, that revealed similar performances under the operating conditions used, a correct and clear distinction between the oxalic acid removal rates using these three samples is not feasible. In fact, two additional CWAQ experiments were performed using a lower catalyst loading (0.040 mg) and, despite the drastic reduction of catalyst amount, samples CNT-BM-M-DT and CNT-BM-U-DT presented similar high performances for oxalic acid oxidation (total removal in 15 min, results not shown). However, it is possible to offer a qualitative discussion about the amount and nature of the N-functionalities introduced on the carbon structure and their consequent effect on oxalic acid degradation. All the prepared samples revealed the presence of three types of N-groups (quaternary nitrogen, N-Q; pyrrole, N-5; and pyridinic, N-6), according to the deconvolution of their respective N1s spectra (Fig. 2). However, the three most active samples presented high N contents (between 0.8 and 4.8%) and also a high relative % of N-6 groups (between 47 and 60%). Based on these contributions and some considerations taken from the literature (presented below), it seems that higher percentage of N-6 groups may be more adequate for this application.

The catalytic activity of N-containing carbon materials is often associated with their basic properties, but other effects, as electron donation, may also enhance the activity of N-doped carbon materials [40]. In fact, it has been reported in the literature that the electronic interaction of oxygen with nitrogen-containing surface groups is high and, consequently, more active oxygen species can be generated [36,39,41,42] to react with the adsorbed organic compounds leading to the oxidation of the organic pollutants. This may be due to the transfer of electrons from the catalyst to the adsorbed oxygen originating highly reactive oxygen species [40]. Pyridine-like N groups are electron rich structures [43]: they have six  $\pi$  electrons plus an unshared pair in a nitrogen  $sp^2$  orbital; therefore, the unshared pair can be used to form radical species and, since the unshared pair is not involved in the  $\pi$  system, the aromatic character of the ring is not much affected. This could also explain the stability of the group after the reaction, no significant changes

being observed in the N-6 group. In the case of N-Q functionalities, this group also increases the electron density of the surface, but their electrons are involved in the conjugation of the  $\pi$  system, and therefore, their ability to donate electrons to the oxygen molecules to form the reactive species should be lower than in the case of N-6 groups. Similar reasoning occurs in the presence of pyrrolic-like groups, the unshared pair of electrons being involved in the  $\pi$  system. In this case, to act as an electron donor, the aromaticity of the molecule has to be sacrificed. Besides the different contributions, the incorporation of N-functionalities on the carbon surface contributes to increase the electronic density of the  $\pi$  system and to improve the surface basicity, leading to higher catalytic activity, which may follow an electron donation reaction mechanism. These considerations also could justify some situations in which it was observed that the reaction mechanism did not involve hydroxyl radicals in the liquid phase when N-doped carbon materials were used in the CWAQ for oxalic acid mineralization [8,36], suggesting that the oxidation reaction can occur by an alternative surface reaction mechanism, possibly as described above.

### 3.2.2. Catalytic ozonation

The experimental results corresponding to the oxalic acid decay during COZ are depicted in Fig. 3. All experiments were followed during 5 h. As can be observed in Fig. 3a, introduction of the prepared catalysts into the ozonation system clearly enhances oxalic acid mineralization. The ball milling process improves the catalytic performance of the CNT (see Fig. 3a) in COZ, as also observed in CWAQ. This result is in agreement with those obtained in a previous study [22].

CNTs doped with nitrogen by the novel methodology [27] were compared with those obtained using undoped CNTs (samples CNT-O and CNT-BM). Fig. 3a shows that CNTs prepared with melamine by dry treatment (CNT-BM-M-DT sample) lead to a faster oxalic acid removal than the CNT-O or CNT-MB samples. These results indicate that the N-groups incorporated onto the CNTs surface by dry treatment improve the catalytic activity of the ball milled CNTs. For comparative purposes, an adsorption experiment using the best ozonation catalyst was performed (O<sub>2</sub> + CNT-BM-M-DT experiment). It was observed that adsorption scarcely contributes to the removal of oxalic acid (11% after 5 h) compared to the catalytic ozonation in the presence of the same sample. The influence of the thermal treatment at 600 °C applied after the ball milling process on the performance of the catalysts was also investigated (Fig. 3a). Although CNT-BM-M-DT-w/o TT presents a nitrogen content twice that found on the surface of the thermally treated sample (9.6% against 4.8% obtained by XPS [27], for CNT-BM-M-DT-w/o TT and CNT-BM-M-DT, respectively), the catalytic performance of the former is lower. The underperformance observed for the sample without thermal treatment (CNT-BM-M-DT-w/o TT) is explained by the fact that all nitrogen present on the sample surface corresponds to the presence of melamine (C=N—C and C—NH<sub>2</sub> bonds), according to the deconvolution of N1s XPS spectrum obtained [27].

This observation proves that the N-functionalities (N-Q, N-5 and N-6 groups) introduced on the carbon matrix by the decomposition of pure melamine during the thermal treatment until 600 °C play an important role in the catalytic activity of the CNTs. Consequently, it can be concluded that the thermal treatment until 600 °C is a fundamental step in the preparation of the N-doped samples, as it was already observed in the case of CWAQ.

Samples prepared by dry, external and wet treatments using urea or melamine as N-precursor were also tested as ozonation catalysts. Although the CNTs prepared with urea present lower N amounts than those prepared with melamine, no significant differences are observed between the catalytic performances of the samples prepared by the same methodology using the different N-precursors (urea or melamine), as can be observed in Fig. 3b (comparison between CNT-BM-M-DT and CNT-BM-U-DT), Fig. 3c (comparison between CNT-BM-M-E and CNT-BM-U-E) and Fig. 3d (comparison between CNT-BM-M-WT and CNT-BM-U-WT). Even though the N-groups positively contribute to the reaction mechanism of COZ, these observations show that the presence of high amounts of N-groups on the CNTs surface is not mandatory. Since the CNTs prepared by the same methodology present similar specific surface areas regardless the N-precursor used (see Table 1), the obtained results suggest that the specific surface area plays an important role in the mineralization of oxalic acid.

Regarding the preparation method (dry, wet or external), CNTs prepared by dry or external treatments lead to a faster oxalic acid removal (around 90% is obtained after 3 h of reaction, Figs. 3.b and 3.c) than the wet prepared samples (around 74% oxalic acid conversion after 3 h of reaction, Fig. 3d). It indicates that the use of solvent during the ball milling step is not advantageous for the oxidation process. The observed negative effect of the solvent on the catalytic activity may be explained in terms of two contributions:

- i) lower N-content, since the dissolution of the N-precursor in the solvent (ethanol) inside the ball mill restricts the contact between the precursor and the CNTs, as already discussed in detail in a previous paper [27];
- ii) textural properties of the CNTs, which practically are not changed by addition of the solvent during the ball milling treatment compared to the original CNT sample: similar pore size distribution and specific surface areas (285 and 291 m<sup>2</sup> g<sup>-1</sup> for CNT-BM-M-WT and CNT-O, respectively (see Table 1)). Since the presence of solvent in the ball milling step prevents the breaking of the CNTs [27],  $S_{BET}$  is lower than the remaining ball milled samples, and consequently, the surface area available for the adsorption and reaction of oxalic acid is lower, contributing to the lower catalytic performance.

A similar trend for the catalytic performance of the N-doped samples was observed for both AOPs studied. However, the difference is more marked in the case of CWAQ. In the case of COZ, the nitrogen functionalities seem to contribute for the increase of the carbon surface reductive character and, therefore, to enhance the transformation of ozone into highly active oxygenated species [44,45]. However, the base strength of the nitrogen groups is not very strong, and one would not expect a strong effect for reactions run at ambient temperature [40].

It should be stressed that, in the present work, the amount of catalyst was reduced to half of that used in previous works [22,46] and the oxalic acid concentration was increased five times in an attempt to make it easier to observe the differences in the catalytic performances of the studied materials.

Taking into account these and the CWAQ results, and that CNT-BM-M-DT combines an easy and simple preparation method without solvent with high amount of N-functionalities, this sample was selected for recycling experiments, with the purpose of

investigating its eventual deactivation during mineralization of oxalic acid. It was observed that the performance of the catalyst remained constant after three consecutive runs in the ozonation of fresh oxalic acid solutions (see Fig. 3e). This behaviour is the opposite as that obtained for commercial CNT, in which a deactivation of about 22% from first to third run was observed [46]. In a previous study using N-doped carbon xerogels, a deactivation of more than 30% after 3 utilizations was observed, which was attributed to oxidized nitrogen species and the lower stability of the N-6 group in carbon xerogels [36]. On the other hand, in a study about the effect of ozone on activated carbons, the surface pyridinic groups were shown to be stable [47]. Therefore, in the present study the stability of the CNT-BM-M-DT sample in the catalytic ozonation of oxalic acid may be due to the stability of the N-6 groups, despite the presence of oxidized nitrogen species introduced by exposure to ozone, as reported in other works [36,40,47].

In summary, regardless of the N-precursor (urea or melamine), the dry treatment proved to be an adequate method to prepare N-doped CNTs with high activity in the COZ processes, having as advantages the fact of being an easy and simple handling method (since it is performed in only one step without using solvents) and the fact that it produces more stable catalysts. Concerning the nature of the N-groups, the N-6 groups were found to be those mainly responsible for the high performance of the N-doped samples in the COZ process [36,48], similarly to what occurs in the CWAQ as discussed in detail above (Cf. Section 3.2.1 CWAQ).

#### 4. Conclusions

The simple post-doping method developed allows the incorporation of large amounts of N-groups, namely, quaternary nitrogen (N-Q), pyrrolic (N-5) and pyridinic (N-6) groups and also allows obtaining metal-free catalysts which are able to effectively mineralize organic pollutants by advanced oxidation processes. All prepared samples show high catalytic performance during the oxidation of oxalic acid, this behaviour being more marked in the case of CWAQ. The relevance of the thermal treatment at 600 °C for the performance of the CNTs as catalysts in both CWAQ and COZ processes was evidenced. The high performance observed for the N-doped samples seems to be related to the high amount of N-functionalities incorporated into the carbon lattice, mainly as N-6 groups. Cyclic experiments showed a high stability of the N-groups on the CNT surface, keeping the original N-functionalities in their reutilization for both AOPs studied.

The easy and simple one-step method developed to introduce N groups on the surface of carbon materials without using any solvent proved to be a promising solution to prepare N-doped CNTs with high catalytic activity in liquid phase oxidation reactions (such as, CWAQ and COZ).

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